

Recent Developments in the Field of Energetic Ionic Liquids

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Energetic ionic liquids (EILs) are a subset of the rapidly growing field of ionic liquid research. These liquid and stable high-energy materials (HEMs) have many benefits, ranging from ease of manufacture and transportation to enhanced safety, as well as many new applications. This review focuses on the developments in this field from 2005 to 2012, with emphasis on propulsion applications of these new materials. Both bipropellant systems (hypergolic EILs) and monopropellant systems (oxygen balanced EILs) are discussed.

10 Introduction

Ionic liquids (ILs), or molten salts, are defined as ionic pairs with melting points below 100 °C.¹ Operating under the banner of green chemistry, the field first gained interest in the early 1990's: ILs were developed with the successful aim of producing non-volatile and reusable solvents for synthetic applications, as well as developing new electrolytes.² Since then, publications in this field have exponentially increased in volume (Fig. 1) due to the development of new and creative applications for ILs: from sensors,^{3,4} solid state photocells,⁵ and batteries,⁶ to thermal fluids,⁷ lubricants,^{8,9} hydraulic fluids,¹⁰ and ionogels;¹¹ among many others. With the evolution of energetic materials towards the development of new ionic salts,^{12,13} the fields of energetic materials and ILs merged to further diversify military and commercial applications: energetic ionic liquids (EILs) designed for the production of new propellants.

The application of high-energy materials (HEMs) depends on the energy releasing process which follows one of the two major pathways: deflagration or detonation (Table 1).¹⁴ Propellants, which decompose through a thermal process (deflagration), differ from explosives, capable of detonation in which they decompose through a shockwave at supersonic speeds.¹⁵ Propellants, also referred to as deflagrating explosives, release their stored energy in the form of hot gas evolving over a given time frame, ranging from milliseconds to seconds.^{12,15,16} Propellants are employed in a wide spread of military applications, including the launching of projectiles, such as: bullets, rockets and missiles, as well as ejecting pilots. More general classes of propellant applications include fuel-like purposes of driving turbines, moving pistons, and starting aircraft engines, as well as pumping fluids and shearing bolts and wires.¹⁶ Detonation explosives refer to the commonly used term "explosives". These are widely used in industrial and engineering applications, such as: blasting, mining, cratering, and the manipulation of metals by either cutting,

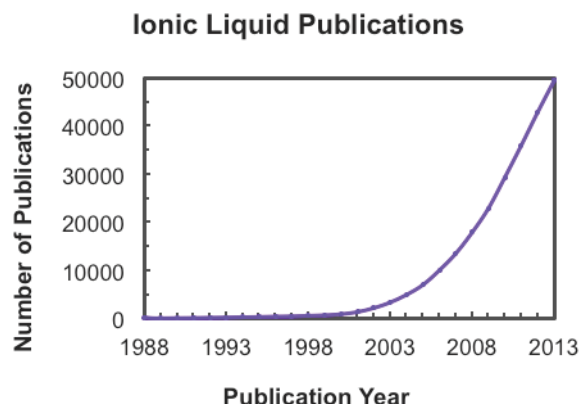


Fig. 1 Exponential curve illustrating the Ionic Liquid field growth. As of August 26th 2013, a search on *SciFinder* using the key words "ionic liquid" generates a list of 49426 publications.

Table 1 Reaction types of an energetic material with $Q_{ex} = 4187 \text{ kJ kg}^{-3}$

Reaction type	Combustion	Deflagration	Detonation
Reaction speed (m s^{-1})	$10^{-3} - 10^{-2}$	10^2	10^4
Mass flow ($\text{m}^3 \text{s}^{-1}$)	$10^{-3} - 10^{-2}$	10^2	10^4
Gaseous products ($\text{m}^3 \text{s}^{-1}$)	1 – 10	10^5	10^{-2}
Reaction time (s m^{-3})	$10^2 - 10^3$	10^{-2}	10^{-4}

Q_{ex} = heat of explosion¹⁴

welding, forming or fragmentation.¹² Military applications make use of shaped charges and the detonation properties of these explosives. Detonation explosives may be divided into two classes: primary and secondary explosives (Table 2).¹⁴ Primary explosives are very sensitive to various initiation stimuli and will detonate regardless of their confinement conditions.¹⁵ Secondary explosives are less sensitive to stimuli but more powerful than primary explosives. The applications listed above utilise secondary explosives for the explosive power, and primary explosives as initiators. Physical properties of some currently employed and well known explosives are reported in Table 3. The boundary between detonating explosives and propellants is however not absolute: under the right conditions, many propellants can behave as detonation explosives.

The intrinsic properties of ILs, such as: low vapour pressures, high thermal stabilities, and low melting points, make them ideal

candidates for minimizing or even eliminating hazardous conditions associated with handling, processing and transporting explosive materials.² In order to achieve low melting points, ILs make use of bulky, asymmetric, poorly packing ions to lower

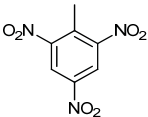
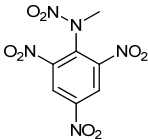
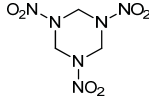
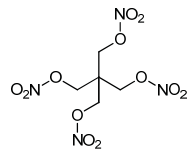
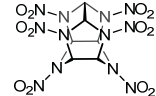

Table 2 Typical sensitivity and performance data for primary and secondary explosives.

	Primary explosives	Secondary explosives
IS (J)	≤ 4	≥ 4

FS (N)	≤ 10	≥ 50
ESD (J)	0.002 – 0.020	≥ 0.1
Q _{det} (kJ kg ⁻¹)	1000 – 200	5000 – 6000
P _{det} (GPa)	---	21 – 39
v _{det} (m s ⁻¹)	3500 – 5500	6500 – 9000

IS = impact sensitivity, FR = friction sensitivity, ESD = electrostatic discharge sensitivity, Q_{det} = heat of detonation, P_{det} = detonation pressure, v_{det} = detonation velocity.

Table 3 Common explosives and their properties.

	TNT ^{14,18,21} 2-methyl-1,3,5-trinitrobenzene	Tetryl ^{15,21} N-methyl-N,2,4,6-tetranitroaniline	RDX ^{14,18,19,21} 1,3,5-trinitro-1,3,5-triazacyclohexane	PETN ^{14,15,21} [3-nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate	CL20 ²¹⁻²⁵ 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitan	Lead azide ^{14,15,21}
						
T _m (°C)	80.4	129.5	204.1	143	167	---
T _d (°C)	295	162	213	202	213	190
T _{ign} (°C)	300	187	210	202	---	327 - 360
T _{det} (°C)	3471	---	4081	4076	---	---
ρ (g cm ⁻³)	1.65	1.73	1.80	1.76	2.044	4.8
OB	-73.96	-47.36	-21.61	-10.12	-10.95	-5.49
N	18.5	24.4	37.8	17.7	38.4	28.9
ΔH _f (kJ mol ⁻¹)	-62.07	33.89	70.29	-530.53	372.00	468.61
ΔH _f (kJ kg ⁻¹)	-273.28	118.02	316.45	-1678.16	848.95	1609.02
ΔH _{det} (kJ mol ⁻¹)	-929.34	-1246.35	-1127.36	-1838.37	-2609.59	-469.00
Q _{exp} (kJ kg ⁻¹)	4091.63	4340.50	5075.50	5815.08	5955.43	1610.36
P _{det} (GPa) ^c	21.0, ^b 20.2 ^a	---	37.5, ^b 34.5 ^a	31.5, ^b 31.1 ^a	48.23	34.3
V _{det} (m s ⁻¹)	6950, ^b 7150 ^a	7080	8750, ^b 8920 ^a	8270, ^b 8660 ^a	9620 ^b	5500
IS (J)	15	3	7.4	3	2 - 4	2.4 - 4
FS (N)	> 353	> 353	120	60	48	< 1
ESD (J)	0.46 - 0.57	---	0.15 - 0.20	0.19	---	0.005

T_m = melting temperature, T_d = decomposition temperature, T_{ign} = thermal ignition temperature, T_{det} = detonation temperature, ρ = density, OB = oxygen balance (for C_aH_bN_cO_d to be converted to CO₂ and H₂O (without crystal water) OB (%) = 1600[(d-2a-b/2)/M_w] where M_w is the molecular weight), N = % nitrogen content, ΔH_f = enthalpy of formation, ΔH_{det} = enthalpy of detonation, Q_{exp} = heat of explosion, P_{det} = detonation pressure, V_{det} = detonation velocity, IS = impact sensitivity, FS = friction sensitivity, ESD = electrostatic discharge sensitivity, ^a calculated value, ^b experimental value, ^c original value

their lattice energy.¹⁷ Favourite choices are quaternary ammonium and N-heteroaromatic cations. The N-heteroaromatic ions have been found to be energetic when combined with appropriate counter ions.¹² This arises from the numerous energetic N–N and C–N bonds which lead to high heats of formation. N-rich ILs have the added benefit of higher densities and better oxygen balance than their carbocyclic analogues, and tend to be more environmentally friendly since their main decomposition product is dinitrogen gas. The composition of energetic ionic liquids (EILs) reported in the literature follows a distinct trend in which ions are employed. The cations generally feature substituted N-heteroaromatic rings or ammonium derivatives: a majority of cations includes imidazolium,²⁶⁻³⁸ triazolium,^{17,18,26,28,31,32,39-45} tetrazolium,^{32,36,39,40,46,47} ammonium,

iminium,^{26,30,48} triazanium,^{39,44} or hydrazinium.⁵⁰⁻⁵² Anions commonly consist of azolates,^{17,27,29,30,38,40,43,44} dicyanamides,^{28,31,34,37,48-50,52,53} dinitramides,^{18,31,45,47,48,54} nitrocyanimides,^{36,48,49,52,53} nitrocyanomethanides,^{32,49} methane-sulfonates,³³ bis(trifluoromethylsulfonyl)imide,³³ picrates,³⁵ nitrates,^{17,18,31,32,34,35,42,45,49,50,53,54} perchlorates,^{17,31,45,47} azides,^{41,48,51} borohydrides,⁵⁵ cyanoborates,^{26,53} or metallic nitro complexes^{39,46} (Fig. 2).

The main focus of EILs has been towards the production of new propellants.⁵⁶ For EILs to be used as propellants, they must exhibit several key characteristics (Table 4). Most importantly, they need to possess high energy density, often found in materials with large positive heat of formation (ΔH_f).⁵⁷ This leads to a high combustion chamber temperature, and in turn a high specific

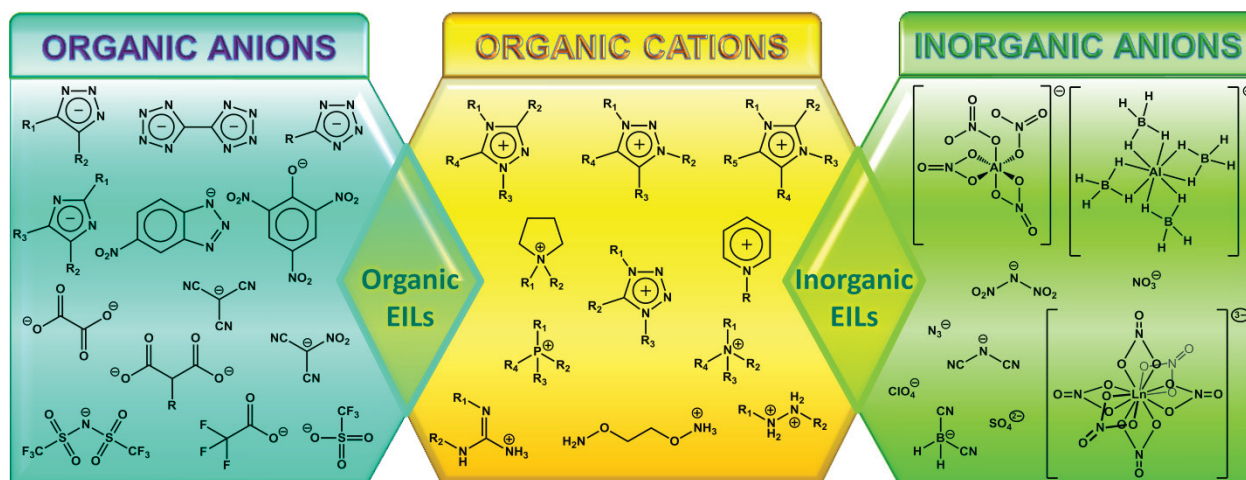


Fig. 2 A selection of choice ions toward energetic ionic liquids.

impulse (I_{sp}) which is a measure of the fuel's efficiency.^{53,57} A propellant's physical properties should include low vapour pressure, low viscosity (η) for facile fuel-oxidizer mixing (in the case of bi-propellant systems), and high bulk density (ρ); all allowing for simpler, more efficient device design.^{26,57} Furthermore, they must exhibit a wide liquid range: low melting point (T_m) and high thermal stability (T_d – decomposition temperature). Evidently, the handling and storage characteristics will play a crucial role in determining the practical use of a given propellant. Important factors to consider are: high resistance to thermal, mechanical (IS – impact sensitivity, FN – friction sensitivity, Table 5) and electrical (EDS – electrical discharge sensitivity) shock, low corrosivity, low toxicity, low fire hazard, no deterioration within storage, inertness with the atmosphere and hydrolytic stabilities.⁵⁷ Other indicators used to determine and characterise the potency of a propellant are detonation pressure (P_{det}), and detonation velocity (v_{det}).

Despite the intensive use of ILs, EILs have been relatively unexplored.^{2,12,58} We herein present a review of recent literature (2005 to 2012) which has focused on propellant applications. For clarity purposes we have divided the aforementioned discussion into bi- and monopropellant sections. Each section is subdivided by the targeted functional properties of the compounds' structure. Due to inconsistencies in the reported properties of new energetic materials (such as simple safety tests, hypergolicity tests, and computational calculations), many were sorted based on their structures.

Bipropellant Energetic Ionic Liquids

Within rocket fuel applications, hydrazine and its derivatives are commonly used in combination with powerful oxidants such as dinitrogen tetroxide (N_2O_4) and white fuming nitric acid (WFNA). Such mixtures are referred to as hypergolic bipropellants, indicating that they ignite upon contact due to an exothermic redox reaction.⁴⁹ With its dangerous (carcinogenic and toxic) properties and high volatility, hydrazine and its derivatives pose many risks in all stages of manipulation, resulting in costly safety procedures.^{26,49} Therefore, much attention has been directed towards producing an alternative to hydrazine, and EILs have taken a lead due to their intrinsic ILs

Table 4 Performance Requirements for EILs²

Physical Properties	
T_m	$< -40\text{ }^\circ\text{C}$
γ	$< 100\text{ dyne cm}^{-1}$
ρ	$> 1.4\text{ g cm}^{-3}$
η	As low as possible
WS	Hydrolytically stable
Hazard Sensitivity	
IS	$> 5\text{ J}$
FS	$> 120\text{ N}$
EDS	$> 5000\text{ V at }0.25\text{ J}$
Thermal Stability	
T_d	$> 150\text{ }^\circ\text{C}$
Isothermal (75°C)	$< 1\text{ \% loss over }24\text{ h}$
Thermodynamic Properties	
ΔH_f	As positive as possible
ΔH_{com}	$> 25\text{ kJ g}^{-1}$
Toxicity	
LD_{50}	$> 0.5\text{ g kg}^{-1}$
AMES	negative

T_m = melting temperature, γ = surface tension, ρ = density, η = viscosity, WS = water sensitivity, IS = impact sensitivity, FS = friction sensitivity, EDS = electro-static discharge sensitivity, T_d = decomposition temperature, ΔH_f = heat of formation, ΔH_{com} = heat of combustion, LD_{50} = lethal dose 50%, AMES = mutagenic potential test.

Table 5 UN classification for the transport of dangerous goods^{14,59}

	IS (J)	FS (N)
Insensitive	> 40	> 360
Less sensitive	35 - 40	ca. 360
Sensitive	4 - 35	80 - 360
Very sensitive	< 4	10 - 80
Extremely sensitive	---	< 10

properties (very low volatility) significantly decreasing the toxic risk. Various EILs have been found to exhibit hypergolic behaviour. Originally, this behaviour was mainly observed for EILs with dicyanamide and nitrocyanamide anions, leading to the

postulation that the anion was responsible for hypergolic behaviour.²⁶ For hypergolic EILs to successfully replace hydrazine they must exhibit the requirements previously mentioned. In addition, they must possess shorter ignition delay (ID) times than the conditions leading to their own detonation.

Finding a replacement for hydrazine is one of the main goals of researchers in this field. Investigating the conversion of hydrazine, and its derivatives, into EILs was one path explored for finding such an alternative. Sabaté and co-workers used *N,N'*-dimethyl hydrazine dihydrochloride to synthesize a family of four new hydrazinium salts (Fig. 3).⁵⁰ These were all reported to be stable during electrostatic discharge sensitivity tests, and failed to detonate when exposed to a Bunsen burner flame. However, only the nitrate (**1a**) and dicyanamide (**1c**) analogues are classified as ILs, and are potential hypergols. A trend emerged within the series, showing that salts based on fewer oxidizing anions were more resistant to impact and friction, showing no signs of decomposition at the maximum loading for BAM drop hammer and friction tests (maximum loadings IS > 40 J and FS > 360 N).⁵⁹ Such was the case for **1c**, which possessed the largest liquid range of all salts produced at 140 °C; ρ 1.420 g cm⁻³, T_m 37 °C, T_d 180 °C, ΔH_f 2842 kJ mol⁻¹, oxygen balance (OB) -140. Analogues consisting of more oxidizing anions decomposed explosively at lower loadings. Despite failing to detonate when exposed to a flame, **1a** showed a substantial energetic reaction accompanied by a gentle transition from burning to deflagration; ρ 1.582 g cm⁻³, T_m 98 °C, T_d 220 °C, ΔH_f 1029 kJ mol⁻¹, OB -26.⁵⁰ Both have a negative oxygen balance (-26 and -140 respectively).

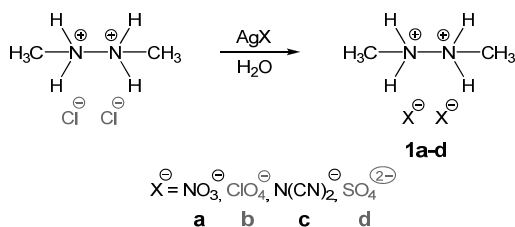


Fig. 3 Reaction scheme for symmetrical dimethyl hydrazine based salts.⁵⁰ Anions in grey correspond to salts which fail to meet the IL designation.

In hopes of achieving larger positive heats of formation, Shreeve and co-workers introduced an extra N-N bond in the cation partner, leading to a family of seven EILs based on a 2,2-dialkyltriazanium cation (Fig. 4).^{49,60} Only four of these EILs (the **2a**, **2b**, **2c**, and **2d** analogues) were found to be hypergolic with either N₂O₄ or WFNA, with **2b** giving the best results; T_m 99.0 °C, T_d 145.6 °C, ID_{N₂O₄} 10 ms, ID_{WFNA} 4 ms, P_{det} 22.2 GPa, v_{det} 8034 m s⁻¹, I_{sp} 228, IS > 60 J. With the second best performance results in this series, the RTEIL **2d** would make a better choice for practical applications; T_m -0.19 °C, T_d 145.7 °C, ID_{N₂O₄} 8 ms, ID_{WFNA} 16 ms, P_{det} 16.0 GPa, v_{det} 7169 m s⁻¹, I_{sp} 226, IS > 60 J. The cation was then proved to play a vital role since the chloride precursor (**2a**) was also found to be hypergolic. Therefore, the anion is not solely responsible for the hypergolic properties as previously expected.^{49,61} This group later developed a series of *N,N*-dimethylhydrazinium EILs (Fig. 5) which paired cations of varying side chain lengths with dicyanamide and nitrocyanamide anions in attempts to investigate which components were most relevant to hypergolicity.⁵² The whole series was found to be

hypergolic with WFNA with IDs ranging from 22 ms to 1642 ms. The authors observed that the nitrocyanamide analogues (**4a-4g**) possessed greater thermal stabilities as well as higher densities, viscosities, and ignition delay times than their dicyanamide analogues. They held the alkyl substituents accountable for trends in the densities and viscosities of both series, with the -CH₂CN (**g**) analogues having the highest values for both properties. Hydrazinium derivatives **3b**, **3d**, and **3e** are the best hypergols with ID times of 22 ms, 24 ms, and 30 ms respectively. **3d** proved to have the overall most desirable properties; T_g < -60 °C, T_d 199.2 °C, ID_{WFNA} 24 ms, P_{det} 9.09 GPa, v_{det} 6057 m s⁻¹, I_{sp} 204.0 s.

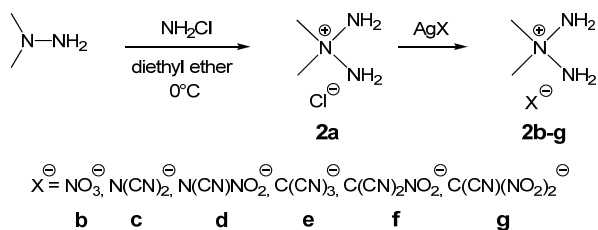


Fig. 4 Reaction scheme for 2,2-dialkyltriazanium based salts.⁴⁹

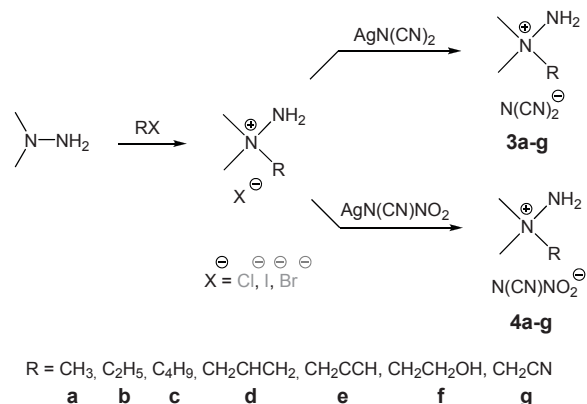


Fig. 5 Reaction scheme for *N,N*-dimethylhydrazinium based EILs.⁵² Anions in grey correspond to salts which fail to meet the IL designation.

Also aiming for high heats of formation, Klapötke and co-workers sought to explore N-rich heteroaromatic compounds. A family of five salts based on aminotetrazoles was synthesized, granting some of the highest nitrogen containing organic substances, yet exhibiting surprisingly high thermal stabilities (Fig. 6 and Fig. 7).^{47,62-66} Only two compounds fall within the ILs characterisation (**5a**, **6c**) with **6c** being the most promising; ρ 1.719 g cm⁻³, T_m 85 °C, T_d 184 °C, $\Delta H_{com-cal}$ -2171 kJ mol⁻¹, $\Delta H_{com-exp}$ -1976 kJ mol⁻¹, ΔH_{det} -1091 kJ mol⁻¹, $\Delta U_{com} \Delta V=0$ -2000 kJ mol⁻¹, OB -25.3, IS 7 J, FS 24 N. With a calculated detonation pressure of 33.6 GPa and a detonation velocity of 8827 m s⁻¹, **6c**

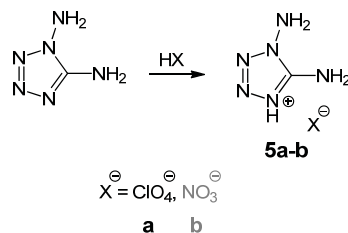


Fig. 6 Reaction scheme for 1,5-diamino-4H-tetrazolium based salts.⁴⁷ Anions in grey correspond to salts which fail to meet the IL designation.

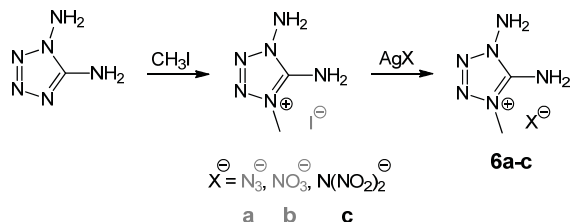


Fig. 7 Reaction scheme for 1,5-diamino-4-methyl-tetrazolium based salts.⁴⁷ Anions in grey correspond to salts which fail to meet the IL designation.

is comparable to the high explosive RDX ($P_{\text{det}} = 34.7$ GPa, $v_{\text{det}} = 8750$ m s⁻¹).¹⁴ In addition to having similar performance results, **6c** is also comparable in terms of its impact sensitivity to RDX (IS = 7.4 J), and less sensitive when compared to other common explosives including Tetryl (IS = 3 J) and PETN (IS = 3 J).^{14,47}

Unfortunately this EIL exhibited the highest friction sensitivity (FS 24 N) of all the salts produced, making it more sensitive than PETN (FS 60 N). It is, however, more stable than the primary explosive lead azide (FS 1 N).¹⁴ No hypergolic tests were reported for these compounds.

Increasing the nitrogen content of stable room temperature EILs (RTEILs) has proven to be a challenge as N-rich heterocyclic rings generally possess higher melting points for their respective salts.⁴⁴ Shreeve and co-workers also sought to employ 5-aminotetrazole based salts, but rather than utilising it as a weak base, as commonly employed,^{40,67,68,69,70} they used it as a weak acid to provide the anion.⁴⁴ The eight salts published were all found to be stable at room temperature for several months. More impressively, they were all stable in water, even when heated to 100 °C. Only three of these salts are ILs (Fig. 8): **7a** ($T_g -38$ °C, T_d 171 °C, P_{det} 16.4 GPa, v_{det} 7397 m s⁻¹), **7b** ($T_g -24$ °C, T_d 174 °C, P_{det} 18.9 GPa, v_{det} 7334 m s⁻¹), and **7c** (T_m 96 °C, T_d 211 °C, IS > 60 J, P_{det} 20.1 GPa, v_{det} 8149 m s⁻¹).⁴⁴ This resulted in the first 5-aminotetrazolate based family of ILs. Furthermore, **7a** and **7b** fall within the designation of RTEILs; the low melting points being attributed to the asymmetry of the 4-amino-1-alkyl-1,2,4-triazolium cation. As of 2008, **7b** has been the RTEIL with the highest nitrogen content percentage (68% weight). Hypergolic tests are also required for these compounds.

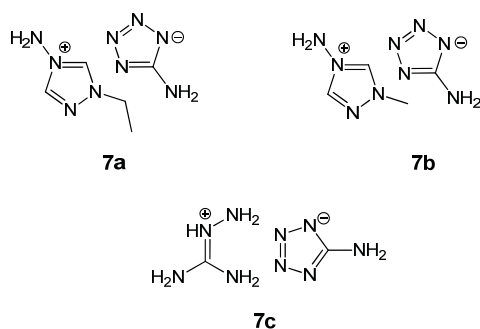


Fig. 8 5-aminotetrazolate based EILs.⁴⁴ **7a** 4-amino-1-ethyl-1,2,4-triazolium 5-aminotetrazolate, **7b** 4-amino-1-methyl-1,2,4-triazolium 5-aminotetrazolate, **7c** aminoguanidinium 5-aminotetrazolate.

A recent example of tetrazolate based EILs has been reported by Pang and co-workers¹⁸ who employed a couple of 1-amino-1,2,3-triazolium based counter-cations (Fig. 9 and Fig. 10). Six of the nine compounds synthesized are ILs and potential hypergols,

though with quite high melting points (> 80 °C). The IL with the lowest melting point, **9c**, has the best oxygen balance and the second best calculated performance values of the series; T_m 82.2 °C, T_d 176.5 °C, OB -10, P_{det} 29.7 GPa, v_{det} 8320 m s⁻¹. The impact sensitivity of **9c** could not be accurately determined due to its deliquescent nature. In comparing the series, it was found that the methyl group on 3-methyl-1-amino-1,2,3-triazole based systems helped to lower the melting point and reduce the impact sensitivity. Furthermore, comparisons with 1,2,3-triazole based systems suggest that incorporating amino groups further assists in lowering the melting point.⁴⁵ Overall, this series was thermally stable, with liquid ranges reaching as far as 100 °C.

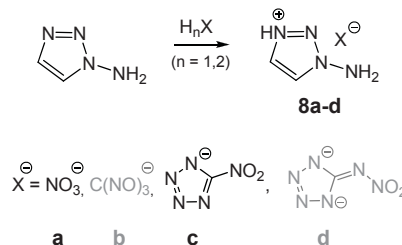


Fig. 9 Reaction scheme for 1-amino-1,2,3-triazolium based salts.¹⁸ Anions in grey correspond to salts which fail to meet the IL designation.

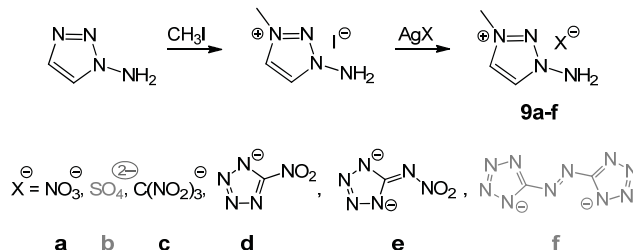


Fig. 10 Reaction scheme for 1-amino-1,2,3-triazolium based salts.¹⁸ Anions in grey correspond to salts which fail to meet the IL designation.

Azido groups embody another alternative to utilise N–N bonds for energy storage: they have been calculated to add approximately 280 kJ mol⁻¹ per azido group to the energy content of a molecule.⁴⁸ Further calculations suggest that the heat of formation of the azide anion in the gas phase (197.2 kJ mol⁻¹) is significantly greater than that of the dicyanamide and nitrocyanoamide anions (113.4 kJ mol⁻¹ and -27.1 kJ mol⁻¹ respectively), which are commonly employed in the design of hypergolic ILs.^{48,49,71,72} Klapötke and co-workers reported several systems outlining the properties of hydrazinium azide based EILs and energetic salts.^{41,51,73-79} Unfortunately, these compounds were volatile and/or hygroscopic materials which also liberated the undesirable and unstable HN₃ elimination by-product. In 2008, Schneider and co-workers introduced triazolium azide based EILs (Fig. 11).⁴¹ Instead of employing AgN₃ to replace the intermediates' halide counter-ion as is common practice, a polymeric quaternary ammonium azide exchange resin was used. This alternative preparative route was deemed safer and easier to perform; however, a 2% ammonium contamination could not be avoided. These new azide EILs, and potential hypergols, were remarkably less sensitive compared to notoriously sensitive covalent azides, and even to RDX (~ 50 kg cm).⁴¹ The 2-azidoethyl-1,2,4-triazolium analogue (**10c**) was found to be stable enough for safe handling. The thermal stability, negligible

volatility and low vapour toxicity for azide-based EILs were attributed to the quaternary nitrogen. The relatively low melting points were attributed to the allyl-, 2-hydroxyethyl-, and 2-azidoethyl functionalities. Unfortunately, the more energetic allyl- and the 2-azidoethyl- side chain functionalities lowered the decomposition temperatures.

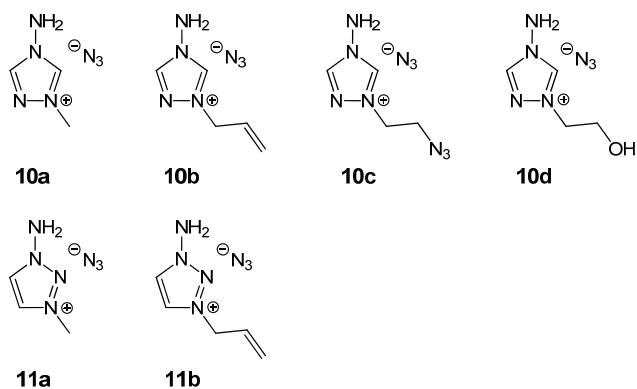


Fig. 11 Triazolium based EILs azides.⁴¹ **10a** 1-methyl-4-amino-1,2,4-triazolium azide, **10b** 1-allyl-4-amino-1,2,4-triazolium azide, **10c** 1-(2-azidoethyl)-4-amino-1,2,4-triazolium azide, **10d** 1-(2-hydroxyethyl)-4-amino-1,2,4-triazolium azide, **11a** 1-amino-3-methyl-1,2,3-triazolium azide, **11b** 1-amino-3-allyl-1,2,3-triazolium azide.

Continuing in the pursuit of higher heats of formations, Shreeve and co-workers set out to synthesize EILs based on 2-azido-*N,N*-dimethylethylamine (DMAZ), an alternative (reduced-

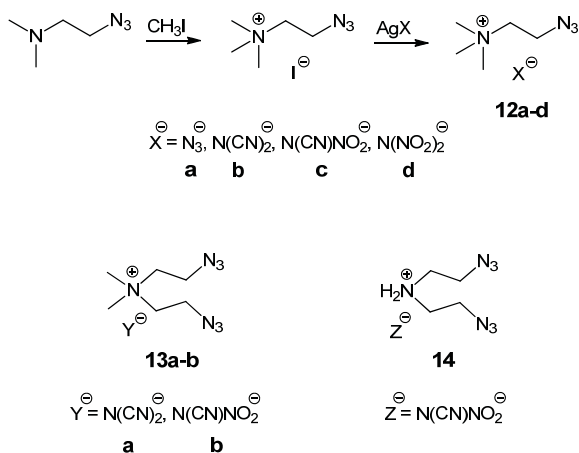


Fig. 12 Reaction scheme for 2-azido-*N,N,N*-trimethylethylammonium based ILs, as well as the *bis*(2-azidoethyl)ammonium and *bis*(2-azidoethyl)dimethylammonium based ILs.⁴⁸ The IL **12b** was also reported by Schneider and co-workers.⁸¹

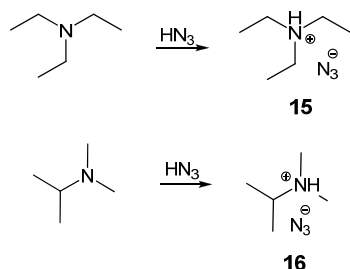


Fig. 13 Reaction scheme for azide anion based ILs; **15** triethylammonium azide and **16** *N,N*-dimethylisopropylammonium azide.⁴⁸

hazard) liquid fuel developed by the U.S. Army, as well as azide counter-anion based ILs (Fig. 12 and Fig. 13).⁴⁸ These azide based EILs were obtained either through metathesis reactions with silver azide or through direct neutralization with hydrazoic acid. Of the eleven salts presented, all but one fall within the IL range, with **12b**, **12c**, **12d**, **13a**, and **13b** classifying as RTEILs. Drop tests with N_2O_4 and WFNA resulted in **12c**, **12b**, **13a**, **13b**, **15**, and **16** exhibiting hypergolicity. Among the RTEILs, **12c** and **13a** possess the shortest ignition delay times for WFNA (8 ms and 16 ms, respectively). With an ignition delay of 8 ms with WFNA, **12c** exhibits the same behaviour as monomethylhydrazine with inhibited red fuming nitric acid (ID_{IRFNA} 8 ms),⁸⁰ displaying promise as a hypergolic propellant. Despite not being RTEILs, **15** and **16** (T_m 80 °C, $\text{IS} > 40$ J, ID_{WFNA} hypergolic, $\text{ID}_{\text{N}_2\text{O}_4}$ explosion, I_{sp} 245 s; and T_m 75 °C, $\text{IS} > 40$ J, ID_{WFNA} hypergolic, I_{sp} 249, respectively) were reported as the first azide-based ILs exhibiting hypergolicity. Both were hypergolic with N_2O_4 , and **15** was found to explode when exposed to WFNA. Both of these compounds are, however, extremely hygroscopic.

Hypergolic redox reactions observed between alkali metal borohydride salts and WFNA in preliminary experiments turned the attention of Shreeve and co-workers toward borohydride based anions: borohydride, cyanoborate and dicyanoborate. Using these anions, several ILs were synthesized but the borohydride and cyanoborate analogues were found to be too water-sensitive for practical applications.²⁶ However, the dicyanoborate based EILs, could themselves be synthesized in water, generating ten new EILs found to be hypergolic with WFNA (Fig. 14). The **17f** analogue possessed the shortest ID times ($T_m < -80$ °C, T_d 189 °C, ID 4 ms) and the **17j** analogue had the lowest viscosity (T_m

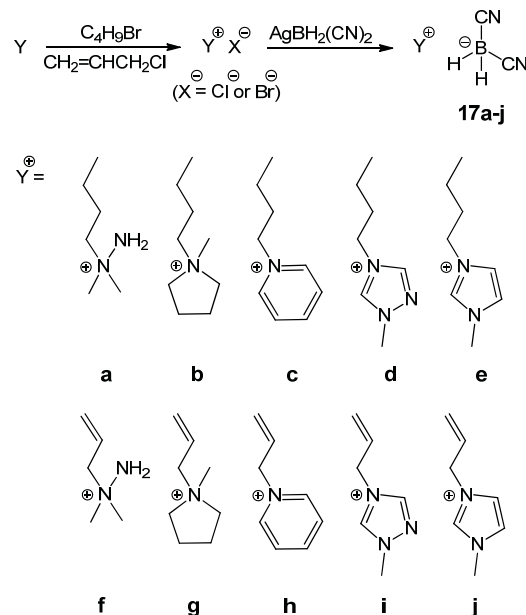


Fig. 14 Dicyanoborate-based EILs.²⁶

< -80 °C, T_d 266 °C, η 12.4 mPa s, ID 8 ms).²⁶ Regardless of the cation, the dicyanoborate analogues exhibited lower melting temperatures, lower densities, lower viscosities and lower ignition delays than their corresponding dicyanamide and nitrocyanamide analogues. The drastic reduction in ignition delay times (81 \rightarrow 28 ms, 130 \rightarrow 4 ms, 46 \rightarrow 8 ms) suggests that the

B–H bond is responsible for the hypergolicity.²⁶ These promising results initiated a shift towards investigating hydride-based anions.

In parallel, searching for the ultimate green rocket fuel alternative, Schneider and co-workers focused not only on the properties of EILs but also on the properties of the oxidizing partner. Hydrogen peroxide was deemed attractive due to its good oxidizing properties, low corrosivity and low vapour toxicity in comparison to WFNA, in addition to environmentally friendly decomposition products.⁵⁵ However, hydrogen peroxide and WFNA are comparable in terms of storage and handling risks.^{82,83} In order to achieve better fuel performance, they utilised an aluminum borohydride anionic complex, taking advantage of the large combustion energies of these light nontoxic metals, while simultaneously providing a large and dense hydride content. This anion was coupled with a trihexyltetradecylphosphonium cation, which would not be reduced by the borohydride components of the anion, unlike the commonly used heterocyclic cations, to give a RTEIL (Fig. 15). It is noteworthy that this EIL is completely stable in air ($T_g -70\text{ }^\circ\text{C}$, $T_d > 150\text{ }^\circ\text{C}$). Drop tests of this EIL into oxidizers resulted in hypergolicity with 90% H_2O_2 (ID < 30 ms), 98% H_2O_2 (ID < 30 ms), N_2O_4 (EIL ignited with the vapours of N_2O_4 prior to the liquids mixing), and WFNA (resulted in explosion rather than combustion).

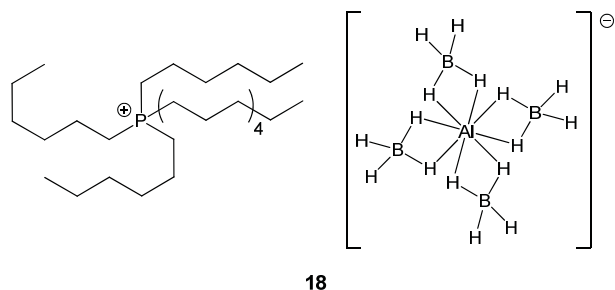


Fig. 15 Aluminum borohydride based EIL.⁵⁵

With boron gaining a lot of attention as a beneficial component of EILs, Rogers and co-workers developed an original approach to include boron nanoparticles suspended in an EIL, using its solvent properties (Fig. 16).²⁸ This technique produced air stable nanoparticles, which were free of the oxide layer (requiring ignition temperatures of $1500\text{ }^\circ\text{C}$) that normally coats boron additives. Milling boron nanoparticles with 1-methyl-4-amino-1,2,4-triazolium dicyanamide (**20**), and dispersing these within the EIL by sonication, led to no significant changes in the ignition delay with respect to the clean hypergolic EIL with WFNA (ID 45 ± 14 ms vs. 37 ± 6 ms). It did, however, result in a shorter, much more intense burn (flame duration 43 ± 4 ms vs. 77 ± 18 ms). A similar experiment was carried out with 1-butyl-3-methylimidazolium dicyanamide (**19**), but led to little enhancement in hypergolicity and a complex burn pattern. Investigations into the surface binding of these ILs to the oxide-free boron nanoparticles found that both the cation and anion of both ILs interacted with the surface.⁸⁴ The ILs differed in the degree of interaction of each species; for **20** the cation's interactions dominated, while for **19** the anion's interactions dominated; the differences being attributed to the amino group of the 1-methyl-4-amino-1,2,4-triazolium cation, which also appeared to induce a thicker capping layer. These results suggest

that the dicyanamide anion is in this case responsible for the hypergolicity, and the strong anionic interactions with the nanoparticles will negatively affect performance. For these additives to be beneficial, the cation's coordinative capabilities need to dominate and secure a thicker capping layer.

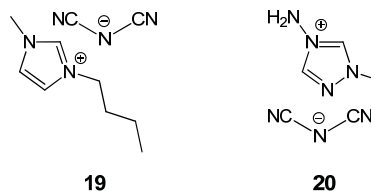


Fig. 16 EILs doped with boron nanoparticles.²⁸

Another, more recent example of utilising the solvent properties of ILs comes from Shreeve et al. (Fig. 17), whom employed ILs to solubilise various boranes. In preliminary tests, the solids: ammonia borane (**a**), hydrazine borane (**b**), and hydrazine bis-borane (**c**) were all found to exhibit hypergolic behavior with WFNA (80, 4, and 12 ms respectively).⁸⁵ Dissolving **a** and **b** in the non-hypergolic IL **21**, resulted in hypergolic solutions (88 and 390 ms respectively). Solutions with known hypergolic EILs **19** (47 ms with WFNA) and **22** (44 ms with WFNA) with all three boranes (**a-c**) proved to all be hypergolic as well. The dissolved boranes reduced the IDs of the EILs significantly, with values ranging from 3 to 34 ms. Assumingly, due to varying solubilities of the boranes in each IL, the authors did not assess the contribution of each borane to the hypergolicity of the resulting liquid. The best performing solutions with IDs of 3 ms were the **19a** and **19b** with mole ratios of 2.70:1 and 2.4:1 respectively.)

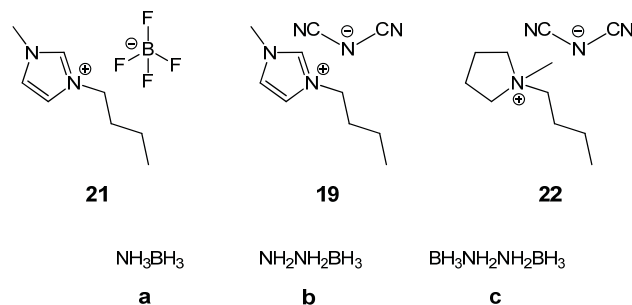


Fig. 17 Ionic liquid solubilized boranes.⁸⁵

Highly reactive B–H bonds led to the incorporation of boron into the cationic partner of EILs, combining this reactivity with the stability and high heats of formation of imidazole rings.⁵³ Of the various EILs achieved (Fig. 18) the **24d** analogue proved to be the most promising; $\rho\text{ }1.05\text{ g cm}^{-3}$, $T_m -80\text{ }^\circ\text{C}$, $T_d\text{ }266\text{ }^\circ\text{C}$, $\eta\text{ }35\text{ mPa s}$, ID_{WFNA} 14 ms, $I_{sp}\text{ }162.4\text{ s}$. Generally, the allyl analogues possess lower melting temperatures, and shorter ignition delay times.

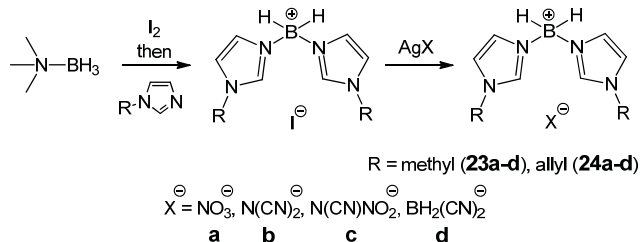


Fig. 18 bis(1-substituted-imidazole-3-yl)dihydroboronium based EILs.⁵³

With the advances over the last decade, hypergolic EILs are showing great promise as replacements for common propellants; such as hydrazine. They have opened new doors towards fuel optimization beyond simple fuel mixing, where solid additives may now be easily incorporated. Targeting N-rich systems, EILs could provide much cleaner sources of fuel, decomposing mainly into N₂. Unfortunately, despite all of the advancements in bipropellant systems, a problem which yet remains is the corrosive nature of the employed oxidants. Thus, in order to find greener fuels, future research must focus on alleviating this problem, likely aiming for milder oxidizers with environmentally friendly decomposition products.

15 Monopropellant Energetic Ionic Liquids

In addition to hydrazine's use as a bi-propellant, its purpose also includes monopropellant applications. The concept of using EILs for monopropellant applications was first suggested by Karl Christe in 1998.⁸⁶ Since then, a few attempts at designing alternative EILs that could act as monopropellants were investigated. The targeted monopropellants, or self-oxidizing EILs, are a beneficial combination of a cationic fuel partner with an oxygen-rich anionic oxidizer, making it unnecessary to resort to external strong oxidants. This reduces the cost related to the use of toxic and corrosive oxidizers, and makes monopropellants suitable for straightforward green applications.

Most known EILs suffer from relatively low oxygen content, resulting in poorer performance than traditional energetic materials.⁴⁶ Even those EILs containing small anions, such as nitrates, perchlorates, and dinitramides, have insufficient oxygen content to completely oxidize their corresponding cations;³⁹ hence EILs must be coupled with powerful oxidizers. Since CO₂ essentially dissociates into CO and O₂ at elevated temperatures (Boudouard equilibrium),⁸⁷ the best performance may be

achieved, in addition to low molecular weight exhaust gas products, by oxidizing the carbon content to CO rather than CO₂.⁴⁶ EILs with such an oxygen balance (OB_{CO} = 1600[(d-a-b/2)/M_w] where M_w is the molecular weight for a compound with formula C_aH_bN_cO_d vs. OB_{CO2} = 1600[(d-2a-b/2)/M_w] could be potential monopropellants. In addition to removing the need for corrosive oxidants such as WFNA, this class of compounds benefits from enhanced stability. In combining fuel in cationic form and an oxidizer in anionic form, a more oxidizer-resistant cation and an anion protected from premature reduction are generated. More specifically, the formal positive charge of the cation increases its ionization potential, while the formal negative charge of the anion decreases its electron affinity.⁴⁶

In 2006, Christe and co-workers produced an oxygen-balanced (OB_{CO}) monopropellant EIL using the tetranitratoaluminate anionic complex and the 1-ethyl-4,5-dimethyltetrazolium cation (ΔH_f free gaseous cation 836 kJ mol^{−1}, anion −1486 kJ mol^{−1}) (Fig. 19).⁴⁶ The anion was selected for its high oxygen content (10.5 of its 12 oxygen atoms are available for reduction), while the cation was chosen due to its high heat of formation and its ability to form ILs. The isomeric mixture (impurities were not

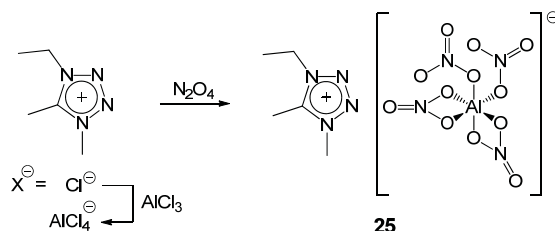


Fig. 19 Tetranitratoaluminate based EIL.⁴⁶

removed since they resulted in a lower melting temperature without affecting the energetic properties) has a glass transition temperature of −46 °C and a strongly exothermic decomposition with onset at 183 °C and maximum at 217 °C. Keeping the EIL at 75 °C for 4 hours results in a 10.4% weight loss, attributed to the loss of NO₂ and O₂, along with the formation of Al-O-Al bridges, as commonly reported for polynitratoaluminates.⁸⁸ A spectacular ignition was achieved using a hot 40-gauge Ni/Cr wire wrapped

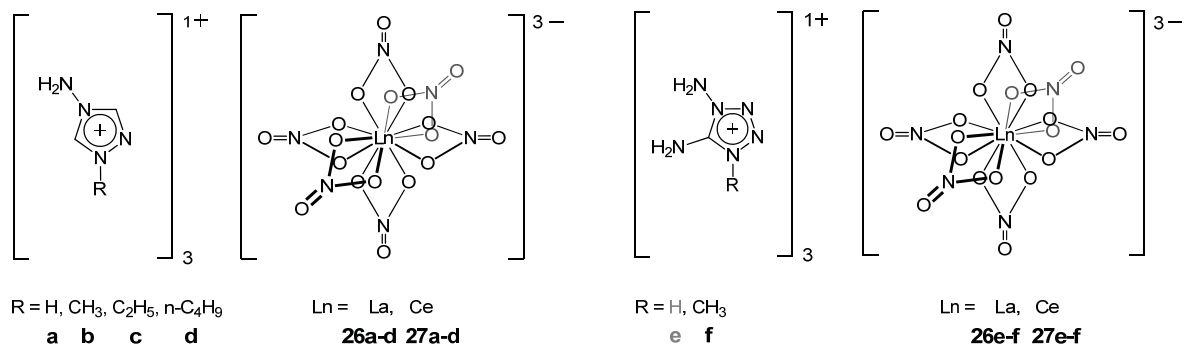


Fig. 20 Hexanitratolanthanate based EILs.³⁹ Anions in grey correspond to salts which fail to meet the IL designation.

around a glass capillary filled with the EIL within a few seconds of applying current, or by heating it to about 200 °C.⁴⁶ The predicted idealized combustion reaction, showing the production of alumina observed upon combustion is:



Unfortunately, EIL **25** was subject to hydrolysis when exposed to water. This problem was overcome by anion substitution from aluminum nitrate to lanthanide nitrate complexes, giving moisture stable EILs; the improved stability being attributed to the strong coordination affinity between lanthanide ions and oxygenated ligands.³⁹ Of the ten ILs synthesized (**26a-f** and **27a-f**, Fig. 20), the **b**, **c**, and **d** analogues (all RTEILs) had a negative oxygen balance (OB_{CO}), while the **a** analogues had a positive oxygen balance. The remaining set, the **f** analogues, were perfectly balanced at zero (OB_{CO}). Despite not being RTEILs, the **a** and **f** analogues easily adopt supercooled phases that only solidify after being stored for days at room temperature. The whole series was found to be hydrophilic and moisture-stable. Heating 1 mg of **26f** to 200 °C led to rapid gas evolution, leaving white lanthanum oxide powder residue, following the reaction:



A main drawback to these two balanced analogues is their impact sensitivity (IS 27 J). Repeating this test six times for **26f** and **27f** led to three and two explosions, respectively.

An original approach to obtaining improved oxygen balance was brought forth by Drake and co-workers who investigated polyoxyamine systems.⁸⁹ Methylene bisoxamine (H₂N-O-CH₂-O-NH₂) based systems showed interesting results, but were far too unstable (unexpected and untimely deflagrations shown by several of their salts). Having postulated that the geminal oxyamines may be unstable under acidic conditions, attention was turned to 1,2-bis(oxyamine)ethane based salts in the hope of generating more robust systems (Fig. 21). Half of the synthesized compounds proved to be ILs, with **29c** qualifying as a RTEIL; T_m < 0 °C, T_d 115 - 120 °C, IS ≤ 20 kg cm, FS < 0.45 kg. However, this RTEIL proved to be very sensitive, having a highly explosive response, completely destroying the scratcher from the Julius

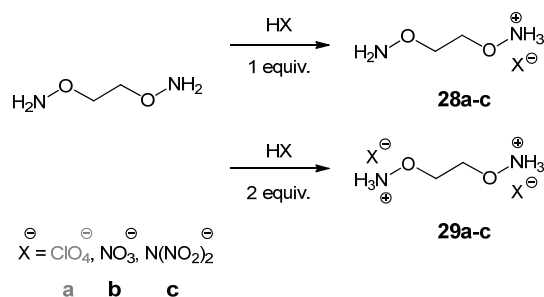


Fig. 21 1,2-bis(oxyamine)ethane based EILs.⁵⁴ Anions in grey correspond to salts which fail to meet the IL designation.

Peters style friction tester. The most stable IL was **28b**; T_m 73-76 °C, T_d 80 °C, IS 94 kg cm, FS 22.8 kg; showing less impact sensitivity (Olin Matheson style drop weight tester with 2 kg mass) than the HMX standard (IS 34 kg cm). Its melting and decomposition temperatures, however, fall short of the desirable values. On the whole, ethylene bis(oxyamine) salts were

extremely sensitive to impact and friction, possessed fairly short liquid ranges which were followed by rapid and highly exothermic decompositions, and were unstable (exhibiting visible changes) even when stored in inert atmospheres. The instability of bis(oxyamine) salts is in contrast to mono-oxyamine (such as hydroxylamine and picryloxamine). Indeed, for the latter, the anhydrous unprotonated species are quite unstable, but the corresponding protonated salts can be stored indefinitely at ambient conditions.^{54,90-92}

In comparison to bipropellant systems, monopropellants have been underdeveloped. Though, in concept, they show great promise as the ultimately green rocket fuel alternative, none of the present systems meet all the required criteria: they are too sensitive to either stimuli or moisture. Further investigations would surely lead to better systems.

A comprehensive comparison of all EILs discussed in this review can be observed in Table 6 as a visual aid, displaying the physical and energetic data available. The most striking observation is the significant lack of uniformity in reporting pertinent physical properties (energetic sensitivity and reactivity) making an objective well-founded comparison of the potential of each EIL challenging.

Table 6 Comparative table of important physical properties of EILs presented in this review.

Compound	ref	ρ (g cm ³)	η^b (mPa s)	T _m (°C)	T _d (°C)	T _{dec} (°C)	ΔH_{cat}^a (kJ mol ⁻¹)	ΔH_{cat}^a (kJ mol ⁻¹)	ΔH_{cat}^a (kJ mol ⁻¹)	ΔH_{cat}^a (kJ mol ⁻¹)	ΔH_{cat}^a (kJ mol ⁻¹)	N ^a	OB ^a	IS (J)	FS (N)	EDS (-) ^x	ID _{WPSA} (ms)	ID ₂₀₄ (ms)	ID ₂₀₂ (ms)	I _{sp}	P _{det} (GPa)	V _{det} (L kg ⁻¹)	V _{exp-gas} (L kg ⁻¹)	Thermal shock	Isothermal (75 °C for 48 h)	
1a	[50]	1.582 ^a	---	98	220	4472 ^U	---	192	U	---	---	30	0	-26	$q > 360$	$q > 360$	$q (-)^x$	---	---	225	24.1 ^U	8117 ^J	893 ^J	---	burns fast	---
	2012	1.420 ^b	---	37	180	2102 ^U	---	552	U	---	---	58	0	-140	$q > 360$	$q > 360$	$q (-)^x$	---	---	199	15.9 ^U	6885 ^J	671 ^J	---		burns slowly
2a	1.47	---	---	---	---	---	756.8 ^k	-230.3 ^k	---	---	---	38	0	-129	q	q	---	nh ^y	26	---	---	---	---	---	---	
2b	1.47	---	---	99.0 ^J	145.6 ^J	---	756.8 ^k	-307.9 ^k	---	---	---	71	0	-70	q	q	---	4	10	---	228	22.2 ⁰	8034 ⁰	---	---	
2c	1.15	---	---	10.7 ^J	134.2 ^J	---	756.8 ^k	113.4 ^k	363.7 ^k	---	---	59	0	-146	q	q	---	22	sh ^d	---	201	12.1 ⁰	6516 ⁰	---	---	
2d	[49]	1.26	---	-0.19 ^J	145.7 ^J	---	756.8 ^k	-27.1 ^k	228.5 ^k	---	---	52	0	-89	q	q	---	16	8	---	226	16.0 ⁰	7169 ⁰	---	---	
	2009	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
2e	1.20	---	---	74.4 ^J	153.3 ^J	---	756.8 ^k	200.3 ^k	465.4 ^k	---	---	51	0	-164	q	q	---	nh ^y	---	190	11.1 ⁰	6207 ⁰	---	---		
2f	1.35	---	---	47.8 ^J	142.5 ^J	---	756.8 ^k	32.2 ^k	296.8 ^k	---	---	45	0	-112	q	q	---	nh ^y	---	211	15.5 ⁰	7009 ⁰	---	---		
2g	1.48	---	---	---	134.2 ^J	---	756.8 ^k	-127.7 ^k	138.2 ^k	---	---	41	0	-70	q	q	---	nh ^y	---	227	21.2 ⁰	7644 ⁰	---	---		
3a	1.10	^c	---	60.5 ^J	253.5 ^J	---	646.5 ^k	113.4 ^k	258.38 ^{kA}	---	---	49.19	-176	^e	---	---	---	58	---	---	189.4 ^J	10.82 ^J	6317 ^J	---	---	
3b	1.06	^c	67.5	30.9 ^J	267.1 ^J	---	613.9 ^k	113.4 ^k	243.66 ^{kA}	---	---	44.36	-191	^e	---	---	---	22	---	---	184.6 ^J	9.79 ^J	6131 ^J	---	---	
3c	1.01	^c	113.9	20.4 ^J	263.3 ^J	---	578.3 ^k	113.4 ^k	232.73 ^{kA}	---	---	38.35	-214	^e	---	---	---	46	---	---	180.0 ^J	8.58 ^J	5932 ^J	---	---	
3d	1.05	^c	78.6	---	199.2 ^J	---	814.6 ^k	113.4 ^k	453.14 ^{kA}	---	---	41.83	-196	^e	---	---	---	24	---	---	204.0 ^J	9.09 ^J	6057 ^J	---	---	
3e	1.13	^c	228.6	---	174.3 ^J	---	909.4 ^k	113.4 ^k	538.55 ^{kA}	---	---	41.46	-189	^e	---	---	---	30	---	---	210.0 ^J	10.08 ^J	6191 ^J	---	---	
3f	1.15	^c	161.8	---	236.0 ^J	---	478.3 ^k	113.4 ^k	109.57 ^{kA}	---	---	40.73	-164	^e	---	---	---	40	---	---	185.8 ^J	10.88 ^J	6281 ^J	---	---	
3g	[52]	1.17	^c	1057.0	---	144.8 ^J	844.9 ^k	113.4 ^k	470.29 ^{kA}	---	---	49.72	-164	^e	---	---	---	1286	---	---	202.1 ^J	11.03 ^J	6318 ^J	---	---	
4a	2010	1.24	^c	35.2 ^J	292.4 ^J	---	646.5 ^k	-27.1 ^k	119.28 ^{kA}	---	---	42.98	-114	^e	---	---	---	126	---	---	213.4 ^J	14.71 ^J	7029 ^J	---	---	
4b	1.17	^c	---	25.4 ^J	296.9 ^J	---	613.9 ^k	-27.1 ^k	105.11 ^{kA}	---	---	39.04	-132	^e	---	---	---	198	---	---	208.0 ^J	12.56 ^J	6681 ^J	---	---	
4c	1.11	^c	119.5	9.0 ^J	285.5 ^J	---	578.3 ^k	-27.1 ^k	93.49 ^{kA}	---	---	34.10	-161	^e	---	---	---	228	---	---	201.2 ^J	10.89 ^J	6408 ^J	---	---	
4d	1.16	^c	84.9	---	208.2 ^J	---	814.6 ^k	-27.1 ^k	314.50 ^{kA}	---	---	36.82	-141	^e	---	---	---	130	---	---	221.5 ^J	12.19 ^J	6596 ^J	---	---	
4e	1.21	^c	269.8	---	189.3 ^J	---	909.4 ^k	-27.1 ^k	403.69 ^{kA}	---	---	37.47	-134	^e	---	---	---	134	---	---	227.2 ^J	12.78 ^J	6611 ^J	---	---	
4f	1.26	^c	185.9	---	269.1 ^J	---	478.3 ^k	-27.1 ^k	-28.68 ^{kA}	---	---	36.29	-113	^e	---	---	---	247	---	---	206.2 ^J	14.09 ^J	6880 ^J	---	---	
4g	1.28	^c	1310.0	---	193.5 ^J	---	844.9 ^k	-27.1 ^k	333.24 ^{kA}	---	---	44.22	-112	^e	---	---	---	1642	---	---	220.4 ^J	14.52 ^J	6899 ^J	---	---	
5a	[47]	1.902 ^a	---	97	192	---	---	192.0 ^{LM}	-959 ^J	---	---	-833 ^J	41.5	-5.5	7	60	---	---	---	---	32.2 ^K	8383 ^K	---	---		
6c	2005	1.719 ^a	---	85	184	---	---	169.0 ^{LA}	-899 ^J	---	---	-989 ^J	56.4	-25.3	7	24	---	---	---	---	33.6 ^K	8827 ^K	---	---		
7a	1.39 ^c	---	---	-38 ^d	171 ^g	---	828.2 ^k	---	523.4 ^k	---	---	63.92	-126	^e	---	---	---	---	---	---	16.4 ^z	7397 ^z	---	---		
7b	[44]	1.44 ^c	---	-24 ^d	174 ^g	---	866.7 ^k	---	546.0 ^k	---	---	68.82	-109	^e	---	---	---	---	---	---	18.9 ^z	7334 ^z	---	---		
7c	2008	1.49 ^a	---	96	211 ^g	---	646.7 ^k	---	302.3 ^k	---	---	79.21	-86	q	---	---	---	---	---	---	20.1 ^z	8149 ^z	---	---		
8a	1.64 ^a	---	---	98.6	177.7	---	972.1 ^k	-306.4 ^k	119.3 ^k	---	---	47.6	-16	21.5 ^r	---	---	---	---	---	---	30.5 ^K	8366 ^K	---	---		
8c	1.75 ^b	---	---	98.8	200.8	---	972.1 ^k	112.8 ^k	577.1 ^k	---	---	63.3	-28	3.1 ^r	---	---	---	---	---	---	27.0 ^K	7948 ^K	---	---		
9a	1.69 ^b	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
[18]	1.59 ^a	---	---	87.0	241.8	---	951.6 ^k	-306.4 ^k	116.4 ^k	---	---	43.5	-35	28.9 ^r	---	---	---	---	---	---	23.7 ^K	7596 ^K	---	---		
2012	1.59 ^b	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
9c	1.57 ^a	---	---	82.2	176.5	---	951.6 ^k	-247.7 ^k	234.1 ^k	---	---	39.4	-10	---	---	---	---	---	---	---	29.7 ^K	8320 ^K	---	---		
1.70 ^b	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
1.59 ^a	---	---	---	92.6	224.3	---	951.6 ^k	112.8 ^{kA}	574.0 ^k	---	---	59.2	-41	3.4 ^r	---	---	---	---	---	---	23.1 ^K	7509 ^K	---	---		
1.59 ^b	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	

Compound	ref	ρ (g cm ⁻³)	η^b (mPa s)	T_m (°C)	T_d (°C)	T_{dec}^a (°C)	ΔH_{cal}^a (kJ mol ⁻¹)	ΔH_{melt}^a (kJ mol ⁻¹)	ΔH_{comb}^a (kJ mol ⁻¹)	ΔH_{het}^a (kJ mol ⁻¹)	ΔU_{comb}^b (kJ mol ⁻¹)	N^a	OB ^a	IS (J)	FS (N)	EDS	ID _{FTIR} (ms)	ID ₂₉₄ (ms)	ID ₂₀₂ (ms)	I_p^a (GPa)	P_{het}^a (m s ⁻¹)	V_{exp}^a (L kg ⁻¹)	Thermal shock	Isothermal (75 °C for 48 h)
9e		1.56^a 1.57^b	89.6	197	---	---	951.6 ^k	386.1 ^k	1056.8 ^k	---	---	60.1	-59 [*]	6.9 [†]	---	---	---	---	---	---	23.0 ^κ	7524 ^κ	---	---
10a		---	43	129	1	---	---	---	569	$i_m-2751.67^{lm}$	---	70	0 ⁻¹⁰⁸ ^e	>20 ^{ts}	>360 [‡]	---	---	---	---	---	---	---	---	---
10b		---	-57	41	109	1	---	---	674	$i_m-3930.85^{lm}$	---	59	0 ⁻¹⁴⁹ ^e	13 ^{ts}	---	---	---	---	---	---	---	---	---	---
10c	[41] 2008	---	---	106	1	---	---	---	933	$i_m-3660.66^{lm}$	---	71	0 ⁻⁹⁸ ^e	>15<20 ^{ts}	---	---	---	---	---	---	---	---	---	---
10d		---	-50	41	129	1	---	---	389	$i_m-3251.25^{lm}$	---	57	0 ⁻¹⁰⁸ ^e	17 ^{ts}	353 [‡]	---	---	---	---	---	---	---	---	---
11a		---	50	156	1	---	---	---	623	$i_m-2810.72^{lm}$	---	70	0 ⁻¹⁰⁸ ^e	>20 ^{ts}	>360 [‡]	---	---	---	---	---	---	---	---	---
11b		---	-62	41	114	1	---	---	724	$i_m-3979.81^{lm}$	---	59	0 ⁻¹³⁹ ^e	<6 ^{ts}	---	---	---	---	---	---	---	---	---	---
12a		1.22 ^c	92	139	1	---	---	---	578	---	---	55.80	-154 [‡]	>40 ^q	---	---	nh [‡]	nh [‡]	227 [†]	---	---	---	---	---
12b		1.15 ^c	9	235	1	---	---	---	518	---	---	48.01	-168 [‡]	>40 ^q	---	---	20	nh [‡]	202 [†]	---	---	---	---	---
12c		1.24 ^c	28	245	1	---	---	---	380	---	---	43.73	-123 [‡]	>40 ^q	---	---	8	nh [‡]	218 [†]	---	---	---	---	---
12d		1.36 ^c	RT	219	1	---	---	---	251	---	---	40.15	-85 [‡]	>40 ^q	---	---	nh [‡]	231 [†]	---	---	---	---	---	---
13a	[48] 2010	1.21 ^c	RT	222	1	---	---	---	894	---	---	54.98	-147 [‡]	>40 ^q	---	---	nh [‡]	16 [†]	221 [†]	---	---	---	---	---
13b		1.32 ^c	RT	222	1	---	---	---	752	---	---	50.16	-113 [‡]	>40 ^q	---	---	nh [‡]	226 [†]	231 [†]	---	---	---	---	---
14		1.41 ^c	58	162	1	---	---	---	777	---	---	57.83	-86 [‡]	>40 ^q	---	---	nh [‡]	245 [†]	245 [†]	---	---	---	---	---
15		1.01 ^c	80	sublimates	---	---	---	---	457	---	---	34.53	-222 [‡]	>40 ^q	---	---	hyper [‡]	expl [‡]	245 [†]	---	---	---	---	---
16		0.99 ^c	75	sublimates	---	---	---	---	430	---	---	37.80	-209 [‡]	>40 ^q	---	---	hyper [‡]	nh [‡]	249 [†]	---	---	---	---	---
17a		0.91 ^c	39.4	<-80	222	1	---	---	---	---	---	30.77	-237 [‡]	---	---	---	6	---	---	---	---	---	---	---
17b		0.92 ^c	22.3	<-80	303	1	---	---	---	---	---	20.29	-267 [‡]	---	---	---	26	---	---	---	---	---	---	---
17c		0.96 ^c	19.8	<-80	252	1	---	---	---	---	---	19.94 ^p	-251 [‡]	---	---	---	18	---	---	---	---	---	---	---
17d		0.99 ^c	29.9	<-80	220	1	---	---	---	---	---	20.90	-215 [‡]	---	---	---	32	---	---	---	---	---	---	---
17e		0.96 ^c	17.3	<-80	307	1	---	---	---	---	---	34.15	-235 [‡]	---	---	---	28	---	---	---	---	---	---	---
17f	[26] 2011	0.93 ^c	35.0	<-80	189	1	---	---	---	---	---	27.45	-222 [‡]	---	---	---	4	---	---	---	---	---	---	---
17g		0.94 ^c	16.6	<-80	259	1	---	---	---	---	---	26.74 ^p	-255 [‡]	---	---	---	8	---	---	---	---	---	---	---
17h		1.00 ^c	13.5	<-80	203	1	---	---	---	---	---	33.74	-238 [‡]	---	---	---	6	---	---	---	---	---	---	---
17i		1.03 ^c	21.0	<-80	217	1	---	---	---	---	---	21.99	-199 [‡]	---	---	---	6	---	---	---	---	---	---	---
17j		0.99 ^c	12.4	<-80	266	1	---	---	---	---	---	22.71	-221 [‡]	---	---	---	8	---	---	---	---	---	---	---
18	[55] 2011	---	---	-70 ^d	>150 ^{ef}	---	---	---	---	---	---	0	-324 [‡]	---	---	---	exp [‡]	hyper [‡]	<30 [‡]	---	---	---	---	no mass loss
19	[20] 2008	1.06	39.14	-6	300	---	---	---	---	---	---	34	-214 [‡]	---	---	---	47	---	---	---	---	---	---	---
with boron nano-particles	[13] 2011	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	44±3 [‡]	---	---	---	---	---	---	---
20	[20] 2008	---	92	-66 ^d	143	---	---	---	---	---	---	59	-131 [‡]	---	---	---	31	---	---	---	---	---	---	---
with boron nano-particles	[13] 2011	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	45±14 [‡]	---	---	---	---	---	---	---

Compound	ref	ρ (g cm ⁻³)	η^b (mPa s)	T_m (°C)	T_d (°C)	T_{det}^a (°C)	$\Delta H_{f,cal}^a$ (kJ mol ⁻¹)	$\Delta H_{f,exp}^a$ (kJ mol ⁻¹)	$\Delta H_{f,com}^a$ (kJ mol ⁻¹)	ΔH_{det}^a (kJ mol ⁻¹)	ΔU_{com}^b (kJ mol ⁻¹)	N^a	OB ^a	IS (J)	FS (N)	EDS (ms)	ID _{NRSA} (ms)	ID ₂₀₄ (ms)	ID ₂₀₂ (ms)	I_{sp}^a	P_{det}^a (GPa)	v_{det}^a (m s ⁻¹)	$v_{exp, gas}^a$ (L kg ⁻¹)	Thermal shock	Isothermal (75 °C for 48 h)
26b		1.76 ^c	---	-24 ^d	231 ^f	---	866.6 ^k	-1924.5 ^k	-1487.6 ^k	---	---	31.19 ^p	-5.9 [*]	---	---	---	---	---	---	---	---	---	---	---	---
26c		1.67 ^c	---	-32 ^d	232 ^f	---	828.2 ^k	-1924.5 ^k	-1541.2 ^k	---	---	29.65 ^p	-16.9 [*]	---	---	---	---	---	---	---	---	---	---	---	---
26d		1.59 ^c	---	-33 ^d	229 ^f	---	782.6 ^k	-1924.5 ^k	-1595.8 ^k	---	---	26.98 ^p	-36.0 [*]	---	---	---	---	---	---	---	---	---	---	---	---
26f		2.06 ^c	---	88 ^d	185 ^f	---	974.3 ^k	-1924.5 ^k	-1226.0 ^k	---	---	39.26 ^p	0 [*]	27 ^{uq}	---	---	---	---	---	---	---	---	---	---	---
27a		1.88 ^c	---	76 ^d	212 ^f	---	910.7 ^k	-1911.6 ^k	-1415.4 ^k	---	---	32.85 ^p	6.3 [*]	---	---	---	---	---	---	---	---	---	---	---	---
27b		1.77 ^c	---	-28 ^d	227 ^f	---	866.6 ^k	-1911.6 ^k	-1477.2 ^k	---	---	31.05 ^p	-5.9 [*]	---	---	---	---	---	---	---	---	---	---	---	---
27c		1.67 ^c	---	-33 ^d	228 ^f	---	828.2 ^k	-1911.6 ^k	-1527.4 ^k	---	---	29.61 ^p	-16.9 [*]	---	---	---	---	---	---	---	---	---	---	---	---
27d		1.60 ^c	---	-37 ^d	230 ^f	---	782.6 ^k	-1911.6 ^k	-1585.7 ^k	---	---	26.94 ^p	-35.9 [*]	---	---	---	---	---	---	---	---	---	---	---	---
27f		2.08 ^c	---	90 ^d	187 ^f	---	974.3 ^k	-1911.6 ^k	-1218.3 ^k	---	---	39.20 ^p	0 [*]	27 ^{uq}	---	---	---	---	---	---	---	---	---	---	---
28b		---	---	73-76	80	---	---	---	---	---	---	27.09 ^p	-36 ^e	9 ^{ts}	22.8 ^{ts}	---	---	---	---	---	---	---	---	---	---
28c	[54] 2006	---	---	57-59	75-80	---	---	---	---	---	---	35.17 ^p	-20 ^e	3 ^{ts}	1.5 ^{ts}	---	---	---	---	---	---	---	---	---	---
29c		---	---	<0	115-120	---	---	---	---	---	---	36.60 ^p	5 ^e	≤2 ^{ts}	<0.4 ^{ws}	---	---	---	---	---	---	---	---	---	---

ρ = density, η = viscosity, T_m = melting temperature, T_d = decomposition temperature, T_{det} = detonation temperature, $\Delta H_{f,cal}$ = heat of formation of the cation, $\Delta H_{f,an}$ = heat of formation of the anion, $\Delta H_{f,alt}$ = heat of formation of the salt, $\Delta H_{f,com}$ = heat of combustion, ΔH_{det} = heat of detonation, ΔU_{com} = constant volume combustion energy, N = % nitrogen content, OB = oxygen balance (for $C_xH_yN_zO_wB_uP_vF_gM_h$ to be converted to CO_2 , H_2O , metal oxide and non-metal oxide where appropriate (without crystal water) OB (%) = $1600[(d-2a)-(b-g)/2-3e/2-5f/2-3h/2]/M_w$] where M_w is the molecular weight and M is any metal) $\{^*OB_{oc}$ = oxygen balance (for $C_xH_yN_zO_wB_uP_vF_gM_h$ to be converted to CO , H_2O , metal oxide and non-metal oxide where appropriate (without crystal water) OB_{oc} (%) = $1600[(d-a)-(b-g)/2-3e/2-3h/2]/M_w$] where M_w is the molecular weight and M is any metal), IS = impact sensitivity, FS = friction sensitivity, EDS = electro-static discharge sensitivity (conducted by placing the compounds on a metallic plate and applying the electrostatic discharge of a Tesla coil), P_{det} = detonation pressure, v_{det} = detonation velocity, $v_{exp, gas}$ = volume of gaseous products produced upon detonation, Thermal shock = compounds are exposed to a Bunsen burner flame, Isothermal = upon being kept at a constant temperature of 75 °C for 48 h the compound does not deteriorate. Green indicates that the minimum requirements, as outlined in Table 4, are met.

^a calculated values, ^b measured values, ^c density measured gas pycnometer (25 °C), ^d T_g (glass transition temperature) is reported, ^e DSC/TGA measurement with 5 °C min⁻¹/DSC/TGA measurement with 10 °C min⁻¹, ^f nitrogen ambient atmosphere for measurements, ^g not observed, ^h original value has been converted to units employed in this review for clearer comparison, ⁱ computed using EXPLO5, ^k calculated with G3 method, ^j computed using (MP2), ^m calculated with G2 method, ⁿ heat of formation in solid phase which was estimated from heat of formation in gas phase by using 20 kcal (84 kJ mol⁻¹) as the heat of sublimation - calculated by G2 method, ^o value calculated by authors of this review, ^p found N% by elemental analysis, ^q BAM methods, ^r tested on a type 12 tooling according to the "up and down" method, ^s tested on an Olin Matheson style drop weight tester, ^t 3/6 explosions, ^u 2/6 explosions, ^v friction testing on a Julius Peters-style friction tester reported in friction force (kg), ^w had a highly explosive response destroying the striker or scratcher completely, ^x rough sensitivity to electrostatic discharge using a Tesla coil (ca. 20 kV) where (+) = sensitive and (-) = insensitive, ^y not hypergolic, ^z hypergolic, ^a resulted in explosion rather than combustion, ^h flame duration 130±31 ms, ⁷ flame duration 43±4 ms, ⁸ hypergolic when a second drop of fuel was dropped into N_2O_4 , ⁶ IL ignited with the vapours of N_2O_4 prior to the liquids mixing, ⁵ 90% H_2O_2 , ^u 98% H_2O_2 , ^o computed using Cheetah 6.0, ⁱ computed using Cheetah 5.0, ^k computed using the empirical equations of Kamlet and Jacobs, ⁴ computed using Cheetah 4.0, ⁿ weight loss after 4 h isothermal.

Conclusions

Accompanying the extensive development of the field of ionic liquids (ILs) over the past twenty years, interest has been growing specifically within the area of energetic ionic liquids (EILs).

5 Mainly focused toward the design of viable, powerful alternatives to currently available rocket fuels, ideal EILs need to surpass the basic requirements of ILs (ionic pairs that melt below $-40\text{ }^{\circ}\text{C}$ rather than $100\text{ }^{\circ}\text{C}$), in addition to have interesting energetic properties. The latter requirement involves a good compromise
10 between stability in ambient conditions (air, moisture), relative sensitivity toward certain stimuli and high energy release. In this review we have outlined recent advances in the design and preparation of EILs, along with the energetic data available for these compounds. Inconsistencies in reporting standard energetic
15 data and measurements led to some difficulties in ranking EILs in terms of their energetic potential. Future efforts should be made to fully characterize newly synthesized EILs with standardized tests and consistent measurements.

Reported EILs thus far can be divided into two categories:
20 potential bipropellants (hypergolic systems), and monopropellants (self-oxidizing systems). The first category encompasses a wide range of cations, from N-rich ammonium and hydrazinium to tetrazolium and other cationic N-heteroaromatic rings; as well as various anions, such as nitro and
25 cyano containing or borohydride based anions. The energetic behaviour of such bipropellants requires a reaction with an external oxidizer; some of which tend to be sensitive to ambient oxidative conditions. The second category consists of an ionic pair comprised of a combustible N-rich cation with an oxidizing
30 anion, making these EILs oxygen-balanced and prone to self-oxidation. Due to this advantageous combination, monopropellant EILs are less sensitive toward ambient conditions and do not require the use of an external oxidizer.

Regarding future developments, a major breakthrough for
35 hypergolic systems would be to determine exactly which fundamental property is responsible for hypergolicity. Azides, dicyanamides, borohydrides and even halides have been found to exhibit this behaviour, though these anions do not guarantee a hypergolic reaction. Identifying the route to hypergolicity would
40 lead to a direct and more efficient design of new EIL bipropellant systems, ideally requiring milder and less corrosive oxidizers. The development of new oxidizers may also be an alternative to maximizing the potential of current EILs. Another route to investigate could be the pursuit of new oxidizing catalysts, which
45 would remove the use of stoichiometric oxidizers.⁹⁷ Furthermore, such catalysts could be developed to capitalize on energetic systems which have not exhibited hypergolic behaviour. Conversely, for monopropellant systems, stable and insensitive oxygen-balanced EILs remain elusive. They are nevertheless of
50 great promise due to their self-sufficient energetic behaviour and controlled release of their high energy density. If stable under ambient conditions and not ultra-sensitive, such powerful monopropellants could lead the way toward more efficient green fuel systems of the future. Despite few researchers reporting the
55 viscosity of their new EILs, a common attribute which needs to be rectified prior to the viable applications as propellants would be in lowering the viscosity of these liquids. The average of the

viscosities reported herein is 40 mPa s , while hydrazine and some of its derivatives are comparable to water, which is approximately
60 0.8 mPa s .⁹⁸

Though there is still room for improvement, this field has developed quite well and promises exciting results. Prior to moving forward toward the effective design of EILs, a better understanding of existing systems is necessary. Therefore, efforts
65 should be focused on a profound analysis of the vast pool of established ionic pair combinations: completing the energetic portfolio of each compound, in parallel with computational investigations regarding the dynamics and synergy of the whole system in its environment.

Notes and references

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